



Thermal reaction of sonochemically prepared amorphous Fe/C

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Abstract An amorphous iron/carbon mixture was prepared by sonolysis of ferrocene in diphenylmethane. Heating of the amorphous mixture at 900 or 1200 °C produced nanoparticles, which were then analyzed using Mössbauer spectroscopy, X-ray diffraction, and transmission electron microscopy. The nanoparticles obtained after heating were spherical with diameters of about 50 nm. The sample obtained after heating at 900 °C consisted of α -Fe and Fe₃C, whereas the sample obtained after heating at 1200 °C consisted of α -Fe and γ -Fe. The reaction of the mixture during the heating process was accompanied by the formation of carbon nanotubes catalyzed by the iron or iron carbide nanoparticles.

Keywords Nanoparticle · Amorphous · Iron metal · Iron carbide · Sonochemistry · Carbon nanotube

1 Introduction

Sonochemical synthesis is a useful method for producing nanoparticles or new materials in a solution. Cavitation produces high temperatures and pressures, which decompose the

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reagents in the solution, and the resultant fragments then cool down rapidly to produce nanomaterials. This method has been applied to produce pure noble metal nanoparticles [1]. Iron based particles are very attractive materials because of their electronic and magnetic properties. Preparation of graphene/iron oxyhydroxide hybrid electrode materials has been reported using ultrasonication [2]. Sonolysis of iron ions in an organic solvent tends to produce an amorphous mixture consisting of Fe and C atoms. Thus, heat treatment of the amorphous Fe/C is required for the production of iron carbide nanoparticles. A mixture of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) and diphenylmethane was sonicated, and the precipitates were heated to produce a mixture of Fe metal, Fe_3C and Fe_2O_3 [3]. Iron is very reactive with oxygen, and the production of iron nanoparticles is always accompanied by the formation of iron oxides. We have previously reported the production of amorphous iron carbide by the ultrasonication of ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) in diphenylmethane [4]. We employed reagents that contained no oxygen, and handling was performed under Ar flow using an infrared image furnace to prevent the oxidation of iron. Heating of the amorphous Fe/C at 450 °C for 2 h did not change the composition, and almost the same Mössbauer spectrum was observed as that for the as-prepared amorphous Fe/C. The as-prepared amorphous Fe/C was heated at 600 °C for 2 h to produce nanoparticles that consisted of Fe_3C and $\alpha\text{-Fe}$ [4]. In this work, we analyzed the nanoparticles obtained after heating at higher temperatures (900 and 1200 °C).

2 Experimental

The experimental setup used in this study was almost the same as that described in our previous report [4]. Briefly, a mixture of ferrocene (15 mmol) and diphenylmethane (45 mL) was kept at 20 °C. Ultrasonication was performed with a high-intensity ultrasonic Ti-horn (Branson Sonifier 450, working frequency: 20 kHz, tip diameter: 6.4 mm, immersion depth: 20 mm) under an argon flow for 6 h. The products were centrifuged, washed with hexane under an argon atmosphere and dried under vacuum. The amorphous product obtained was heated at the desired temperature using an infrared image furnace (Ulvac, MILA-5000) under an argon flow for 2 h. The products were investigated using Mössbauer spectroscopy ($^{57}\text{Co}/\text{Rh}$ source), X-ray diffraction (XRD; Rigaku, RINT2000, $\text{Cu-K}\alpha$), and transmission electron microscopy (TEM; Hitachi, H-9500).

3 Results and discussion

3.1 Mössbauer spectra

Sonolysis of ferrocene in diphenylmethane produced a black precipitate. Mössbauer spectra of the precipitate were measured at 293 K (Fig. 1a) and 6 K (Fig. 2a), and showed a paramagnetic doublet due to amorphous Fe/C, as previously reported [4]. As the environment of Fe atoms in amorphous Fe/C is inhomogeneous, the δ and ΔE_q values have distributions. The spectrum measured at 293 K (Fig. 1a) was fitted into two sets of doublets to substitute the distributions. The amorphous Fe/C precipitate samples were heated at 900 or 1200 °C for 2 h under argon. Mössbauer spectra of the heated samples were also measured at 293 K (Fig. 1b,c) and 6 K (Fig. 2b), and the parameters are summarized in Tables 1 and 2.

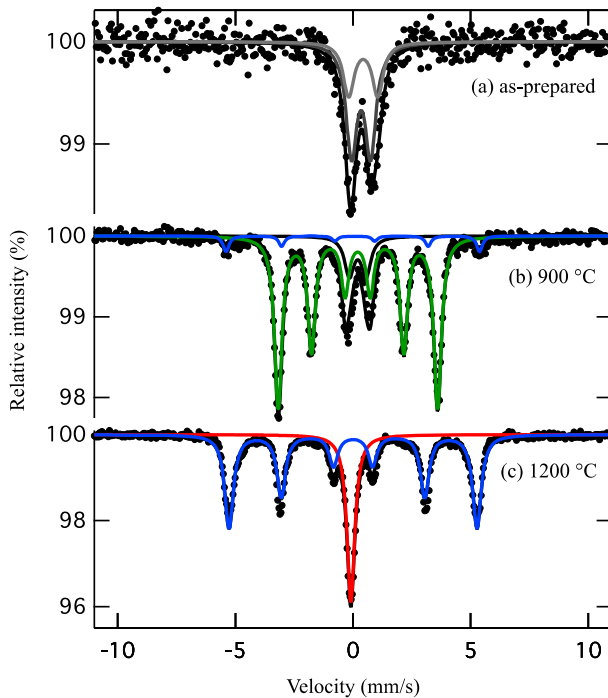


Fig. 1 Room temperature Mössbauer spectra of **a** as-prepared amorphous Fe/C, and samples annealed at **b** 900 °C and **c** 1200 °C

The Mössbauer spectrum of the sample heated at 900 °C and measured at room temperature (Fig. 1b) indicated a mixture of Fe_3C and $\alpha\text{-Fe}$, in addition to a small amount of paramagnetic amorphous Fe/C, which was almost the same as the sample obtained after heating at 600 °C in our previous report [4]. Although a mixture of $\gamma\text{-Fe}$ and C (or $\gamma\text{-Fe}$ and Fe_3C) should be stable at 600 °C according to the conventional phase diagram [5], the sample reached the ' $\alpha\text{-Fe} + \text{Fe}_3\text{C}$ ' phase while cooling down to room temperature.

The sample obtained after heating at 1200 °C for 2 h was a combination of $\alpha\text{-Fe}$ and $\gamma\text{-Fe}$ (Fig. 1c), without any trace of Fe_3C or amorphous Fe/C. The same sample measured at 6 K (Fig. 2b) had a similar spectral pattern with a small difference in isomer shift due to a second-order Doppler shift. From the conventional Fe-C phase diagram, it is considered that $\gamma\text{-Fe}$ with a low carbon concentration (<1.7 wt% carbon) or a liquid phase appears at 1200 °C and the ' $\alpha\text{-Fe}$ and $\gamma\text{-Fe}$ ' phase appears only between 723 and 910 °C in the region of low carbon concentration (<0.8 wt%). It has been reported that the $\gamma\text{-Fe}$ nanoparticles (30–100 nm diameter) did not transform to martensite, because the surface tension plays an important role in the prevention of homogeneous martensitic nucleation [6]. It was found that Fe-C alloys have a tendency towards phase separation at high temperature, which leads to the precipitation of carbon, and $\gamma\text{-Fe}$ and C coexist in this phase [7]. It was presumed that the sample heated at 1200 °C was in the ' $\gamma\text{-Fe} + \text{C}$ ' phase, and that a portion of the $\gamma\text{-Fe}$ then transformed to $\alpha\text{-Fe}$ while cooling down to room temperature; a mixture of $\alpha\text{-Fe}$ and $\gamma\text{-Fe}$ nanoparticles were obtained in the present work.

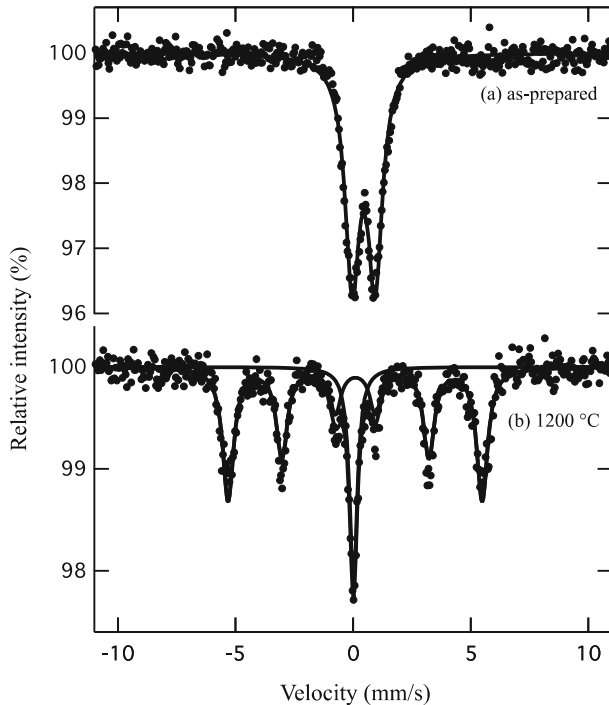


Fig. 2 Mössbauer spectra measured at 6 K of **a** as-prepared amorphous Fe/C and **b** sample annealed at 1200 °C

Table 1 Mössbauer parameters for spectra presented in Fig. 1

Sample		δ (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	H (kOe)	Relative Area (%)
(a) As-prepared	doublet 1	0.34(2)	0.81(5)		67
	doublet 2	0.43(3)	1.23(9)		33
(b) 900 °C	doublet	0.20(2)	0.71(2)		12
	Fe ₃ C	0.20(1)	-0.01(1)	210(1)	83
	α -Fe	0.03(2)	-0.09(4)	334(1)	6
(c) 1200 °C	γ -Fe	-0.09(1)			29
	α -Fe	0.00	0.00	327(2)	71

3.2 XRD patterns

XRD patterns of the samples were measured and the peaks were assigned according to the PDF database [8]. The XRD pattern of the as-prepared sample (Fig. 3a) showed peaks assigned to Ti metal, and no patterns corresponding to iron compounds were observed, which was in agreement with the Mössbauer spectra: amorphous Fe/C does not exhibit XRD peaks. The Ti metal was a contaminant due to erosion of the Ti tip of the ultrasonicator. The XRD pattern for the sample heated at 900 °C (Fig. 3b) showed α -Fe and Fe₃C peaks, and the sample heated at 1200 °C showed α -Fe and γ -Fe peaks. The XRD results were thus in

Table 2 Mössbauer parameters for spectra presented in Fig. 2

Sample		δ (mm s ⁻¹)	ΔE_q (mm s ⁻¹)	H (kOe)	Relative Area (%)
(a) As-prepared	doublet	0.44(1)	0.98(1)		100
(b) 1200 °C	γ -Fe	-0.01(1)			23
	α -Fe	0.01(1)	-0.01(1)	336(1)	77

agreement with the Mössbauer spectra. Beside the iron compounds, Ti metal and graphite or carbon nanotubes (CNTs) were obtained. Although the carbon in the samples heated below 600 °C was amorphous [4], the amorphous carbon changed to graphite or CNTs at temperatures above 900 °C. The Ti metal was also changed to TiC when heated at 900 and 1200 °C.

The Mössbauer spectrum of Ti-Fe alloy with a low iron concentration (0.4 wt% Fe) has been reported to have a singlet peak with an isomer shift of $\delta = 0.0$ mm/s, and spectra for those alloys with higher iron concentrations >2.5 wt% Fe showed doublet peaks with negative isomer shifts [9]. In the present work, no doublets corresponding to Ti-Fe alloy were observed in the Mössbauer spectra. Although the singlet peak assigned to γ -Fe (Figs. 1c and 2b) had a similar δ value to that of the Ti-Fe alloy with a low iron concentration, the XRD pattern for the same sample (Fig. 3c) indicated the presence of γ -Fe and TiC. Therefore, Ti-Fe alloy was not produced in this system. The Ti-metal particles and Fe atoms were dispersed in an excess amount of amorphous carbon prior to heating; therefore, Ti and Fe reacted with the C atoms independently.

3.3 TEM images

TEM observations of the as-prepared sample did not reveal any particles, but only the hazy contrast of an amorphous material (Fig. 4a). The sample obtained after heating at 900 °C consisted of spherical particles with diameters of about 50 nm (Fig. 4b). The Fe and C atoms migrated during heating to form compositions consistent the Fe-C phase diagram, and the particles stabilized while cooling down to room temperature. The sample obtained after heating at 1200 °C consisted of spherical particles with diameters of about 50 nm (Fig. 4c). Besides these particles, CNTs were also observed. The CNTs were not straight, but bent and tangled. It is well known that Fe or Fe₃C nanoparticles acts as a catalyst for the synthesis of CNTs from carbon hydride gas.

Various methods for producing CNT have been reported. The most common synthesis method is thermal chemical vapor deposition (CVD), whereby CO or a hydrocarbon is heated at about 1000 °C with a transition metal catalyst [10]. Sonochemical synthesis of CNTs using liquid chlorobenzene with ZnCl₂ particles (<200 μ m in diameter) has been reported [11]; the hot spot breaks the organic material to produce disordered carbon, and the disordered carbon is then annealed by inter-particle collisions. Here, we report the first study that provides evidence that CNTs can be synthesized by a solid phase reaction of amorphous Fe/C.

3.4 UV-vis spectra of CNTs

To confirm the production of CNTs, the sample was dispersed in an aqueous solution of sodium dodecyl sulfate (SDS) and the UV-vis spectrum (Shimadzu, UV-2600) was

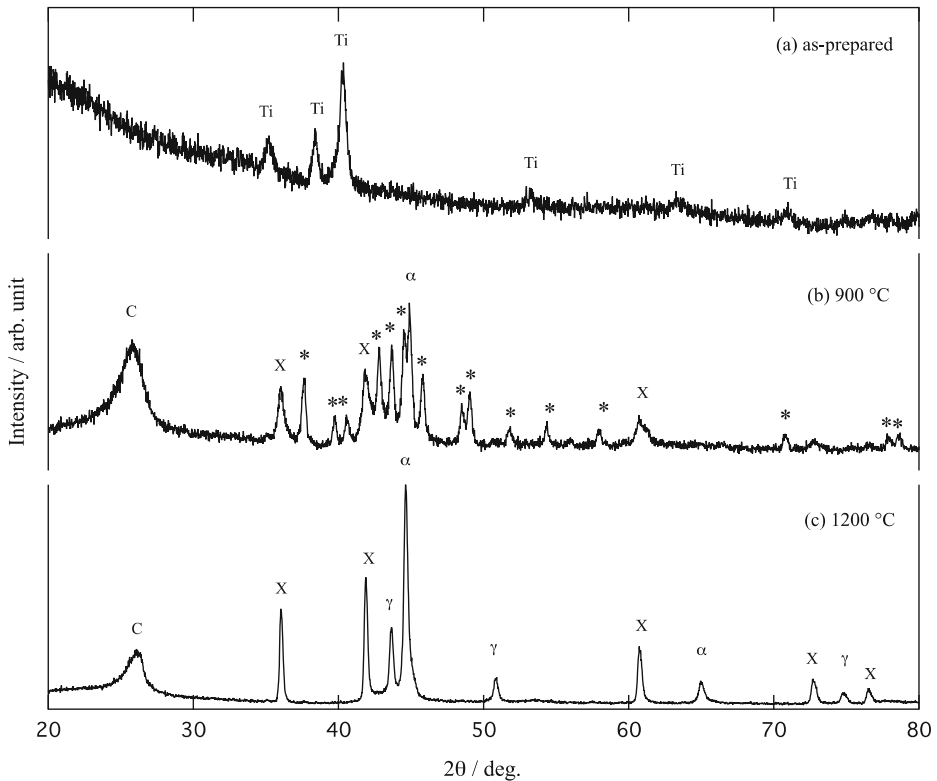


Fig. 3 XRD patterns for **a** as-prepared amorphous Fe/C, and samples annealed at **b** 900 °C and **c** 1200 °C. The Ti, X, C, *, α , and γ labels correspond to Ti metal, TiC, graphite, Fe₃C, α -Fe, and γ -Fe, respectively

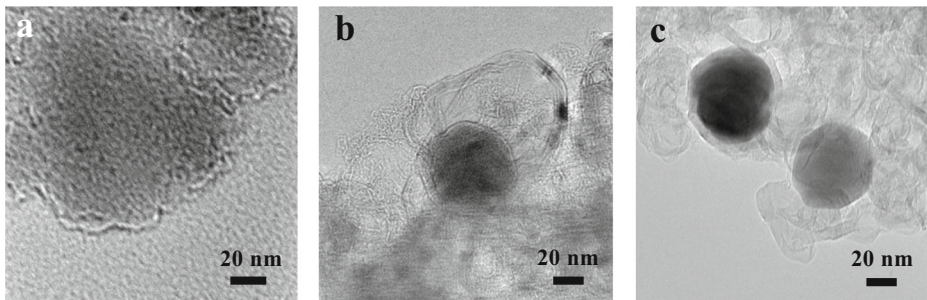


Fig. 4 TEM images of **a** as-prepared amorphous Fe/C, and samples annealed at **b** 900 °C and **c** 1200 °C

measured (Fig. 5). It has been reported that CNT/SDS dispersions are very stable in water [12]. A sample (1 mg) was mixed with SDS (0.2 g) in water (20 mL), homogenized with a conventional low-energy ultrasonic bath for 30 min, and the deposits were then separated by centrifugation. The UV-vis spectrum of the CNT dispersion was measured. Plasmon resonance associated with CNT π electrons has been reported to appear at around 155–310 nm, with an extinction coefficient of about 50 mL/mg-cm, regardless of the CNT structure

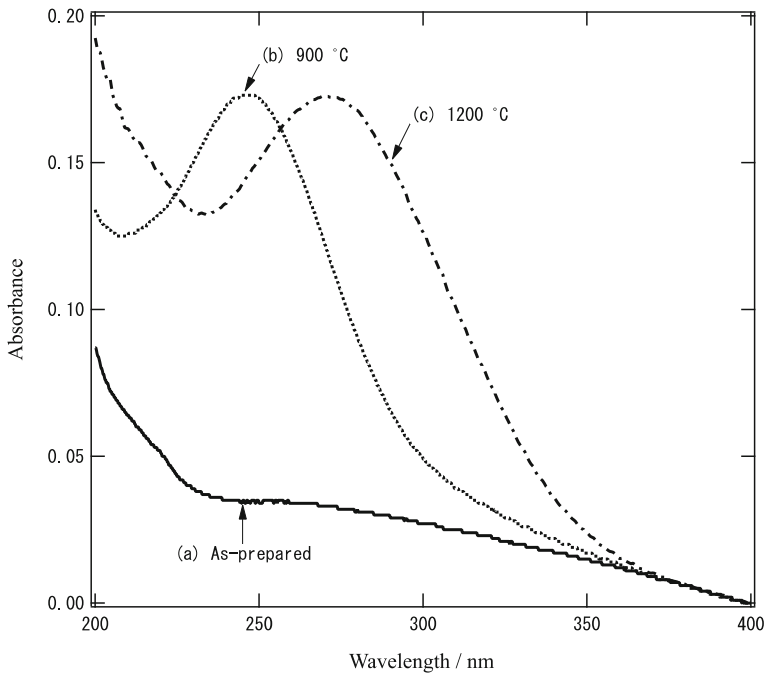


Fig. 5 UV-vis spectra of samples dispersed in SDS: **a** as-prepared amorphous Fe/C, and samples annealed at **b** 900 °C and **c** 1200 °C

(single-walled or multi-walled) [13]. The spectrum of the as-prepared amorphous sample (Fig. 5a) and the samples heated below 450 °C showed broad absorption bands without any peaks around 250 nm. On the other hand, the spectrum of the sample heated at 900 °C had a clear peak at $\lambda_{\max} = 246$ nm (Fig. 5b); the absorbance of the peak after subtracting the baseline was estimated to be 0.14. Assuming that all of the CNTs were dispersed in the solution and that the absorptivity was the same as that reported in the literature [12], the amount of CNTs was estimated to be 0.06 mg. Therefore, of the total mass of the sample containing Fe and C atoms, almost 6% by weight was CNTs. Similarly, the UV-vis spectrum of the CNTs in the sample heated at 1200 °C was measured, and an absorption peak at $\lambda_{\max} = 271$ nm was observed (Fig. 5c). The energy of π plasmons has been reported to become higher with an increasing CNT diameter [13], which suggests that the CNTs obtained by heating at 1200 °C had larger diameters than those obtained at 900 °C.

4 Conclusion

Amorphous Fe/C was produced by ultrasonication of ferrocene in diphenylmethane. Heating of the amorphous product at 900 °C for 2 h produced a mixture of Fe_3C and α -Fe, whereas heating at 1200 °C for 2 h produced a mixture of α -Fe and γ -Fe. The particle sizes obtained at 900 °C and 1200 °C were both about 50 nm. The reaction was accompanied by the formation of CNTs catalyzed by the Fe nanoparticles. Thus, CNTs were synthesized by a solid phase reaction of amorphous Fe/C.

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